6 Electrically rechargeable zinc-oxygen flow battery with high power density

Electrochemistry Communications 69 (2016) 24–27

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Electrically rechargeable zinc-oxygen flow battery with high power density

Marina Bockelmann *, Ulrich Kunz, Thomas Turek

Institute of Chemical and Electrochemical Process Engineering, Clausthal University of Technology, Leibnizstr. 17, Clausthal-Zellerfeld 38678, Germany
Energie-Forschungszentrum Niedersachsen, Am Stollen 19A, Goslar 38640, Germany

ARTICLE INFO

Article history:
Received 21 April 2016
Received in revised form 12 May 2016
Accepted 12 May 2016
Available online 21 May 2016

Keywords:
Secondary zinc–air battery
Three-electrode configuration
Metal foam
Oxygen depolarized cathode
Oxygen evolution catalyst
Alkaline electrolyte

ABSTRACT

The development of a powerful, cyclically stable and electrically rechargeable zinc-oxygen battery with a three-electrode configuration is reported. A copper foam was used as stable substrate for zinc deposition in flowing potassium hydroxide electrolyte, while oxygen reduction and evolution were accomplished by a commercial silver electrode and a nickel foam, respectively. The cell could be charged and discharged with up to 600 mA cm^{-2}, delivered a peak power density of 270 mW cm^{-2}, and performed for more than 600 cycles, although short circuits by dendrite formation could not yet be completely avoided. At a current density of 50 mA cm^{-2} and a temperature of 30 °C, a promising energy efficiency of 54% was achieved.

1. Introduction

In recent years electrically rechargeable alkaline zinc–air batteries received increasing attention and were suggested to be a promising candidate for electrical energy storage. Zinc–air batteries have a high theoretical energy density of 1350 Wh/kg, low costs due to good availability of zinc and are safer than lithium ion batteries [1–3]. However, until now zinc–air batteries have only found technical use as primary cells for low current electrical appliances such as hearing aids, flashing lights or alarm monitoring devices. Despite decades of research and development [4], electrically rechargeable zinc–air cells still suffer from low efficiency and insufficient cyclability. The main problems of secondary alkaline zinc–air batteries are dendritic or mossy growth of zinc resulting in morphology and shape change, self-dissolution and passivation of the zinc electrode during discharge as well as low catalytic activity and lifetime of oxygen electrodes [5–8].

Primary zinc–air batteries with alkaline electrolyte generally contain a gelled mixture of granulated zinc powders as a negative electrode. As a positive electrode for the oxygen reduction reaction (ORR) gas diffusion electrodes on the basis of metal oxides or carbonaceous materials as ORR catalysts are used. For electrically rechargeable zinc–air batteries an additional electrode for the oxygen evolution reaction (OER) or a bifunctional electrode for both oxygen reactions is required. The most technically favorable ORR catalysts in alkaline media so far, platinum or silver, are inapplicable for the oxygen evolution, thus ruthenium oxide and iridium oxide are commonly used for this purpose [9]. Although gelled zinc electrodes known from primary batteries were successfully recharged for a number of cycles [10], these systems suffer from low inter-particle contact after deep discharge [6,11]. For that reason coherent porous zinc electrodes with a better electrical conductivity have to be developed to facilitate rechargeability. Zinc pellets or fibrous zinc electrodes, which have also been proposed, suffer from densification during operation, which leads to dramatic performance decrease [12,13]. On the other hand, densification is much less of a problem if electrochemically stable substrates for zinc deposition are used. The performance of zinc–air batteries is closely related with the composition of the alkaline electrolyte. Potassium hydroxide (KOH) solution with a concentration of 30 wt.% shows the highest ionic conductivity, a good solubility of zinc oxide (ZnO) and relatively low viscosity, which is beneficial for high power density flow battery applications [8].

The most powerful zinc–air systems developed so far contain packed bed zinc anodes or zinc slurries, which can be mechanically or hydraulically refueled after discharge. These systems reached power densities of up to 300 mW cm^{-2}, operated with air at temperatures as high as 70 °C [12,14–19]. Regeneration of zinc particles, however, is only possible in a separate cell, and no detailed information about the cyclability of these systems was provided. Recently, Ma et al. [20] and Li et al. [1] demonstrated a much improved cyclic stability of a rechargeable zinc–air cell of up to 100 cycles with a coherent zinc electrode in a three-

* Corresponding author at: Institute of Chemical and Electrochemical Process Engineering, Clausthal University of Technology, Leibnizstr. 17, Clausthal-Zellerfeld 38678, Germany.
E-mail address: marina.bockelmann@tu-clausthal.de (M. Bockelmann).

http://dx.doi.org/10.1016/j.elecom.2016.05.013
1388-2481/

electrode cell configuration. Li et al. [1] measured a high power density of about 265 mW cm^{-2} with respect to the geometric area of the oxygen electrode. However, these authors emphasized that the developed cell arrangement was not suitable for practical applications since the used zinc electrode was strongly oversized. Furthermore, zinc electrode and electrolyte were replaced during the cycling tests.

In the present contribution we demonstrate an electrically rechargeable alkaline zinc-oxygen flow cell on the basis of copper foam as substrate for zinc deposition and nickel foam for the oxygen evolution reaction combined with a silver-containing oxygen depolarized cathode (ODC). Silver-based ODCs are well-known from their technical use in alkaline fuel cells and chlor-alkali electrolysis [21,22] and exhibit high catalytic activity and excellent long-term stability. The advantages of copper and nickel metal foams are high surface area, good electrical conductivity and electrochemical stability in alkaline solutions. Due to their highly porous and open structure, these foams may be operated in flow-through mode resulting in intimate contact with the electrolyte. As early as 1986, Ross already used metal foams as electrode materials in rechargeable zinc–air batteries and could show a good cyclability of the cell. However, the maximum operating current density was only 20 mA cm^{-2} and this interesting concept received no further attention [23–25]. In contrast to the results obtained by Ross, our cell is able to provide unprecedented high power densities related to the geometric area of the zinc electrode. It shows furthermore an increased lifetime without any exchange of electrodes or electrolyte. In this paper first promising results of proof-of-principle experiments are reported and the future optimization potential of the novel concept is discussed.

2. Material and methods

A commercial copper foam (Alantum) with geometric surface area of 2 cm^2, a thickness of 2.4 mm, a nominal pore size of 800 μm and a porosity of 91% was used as substrate for electrochemical zinc deposition in the testing cell. The copper foam was soldered with tin on a zinc current collector, which was prevented from any contact with electrolyte and therefore did not take part in the reaction. For the oxygen reduction a silver-based ODC (Covestro) with a geometric surface area of 5 cm^2 was applied. As an electrode for the oxygen evolution reaction (OEE) during the charging process, a commercial nickel foam (Inco) with a porosity of 97%, a pore density of 110 PPI, a geometric surface area of 5 cm^2 and a thickness of 1.5 mm was used. All tests were performed in 30 wt.% KOH electrolyte with 2 wt.% ZnO, which corresponds to ca. 50% of the maximum solubility of ZnO in 30 wt.% KOH [26]. The electrolyte tank was continuously supplied with nitrogen in order to prevent the diffusion of atmospheric carbon dioxide into the system and to displace formed oxygen or hydrogen from the electrolyte. The overpotentials of the zinc electrode were measured with a reversible hydrogen reference electrode (RHE) HydroFlex® (Gaskatel), which was placed near the inlet of the cell with a distance of 3 cm to the zinc electrode. The testing flow cell made of acrylic glass allowed a horizontal arrangement of the electrodes, whereas the copper foam was placed on top, followed by the nickel foam and the ODC at the bottom (Fig. 1). The testing cell had dimensions of 32 × 16 × 8 mm, while the gap between the copper foam and the oxygen electrodes was 3 and 5.5 mm, respectively. The volume flow rate of the electrolyte pumped through the cell was set at 0.4 L/min, while the ODC was supplied with pure oxygen at a flow rate of 0.2 L/min. The formed oxygen, and possible small amounts of hydrogen, could be fully removed from the cell by flowing electrolyte during the charging process.

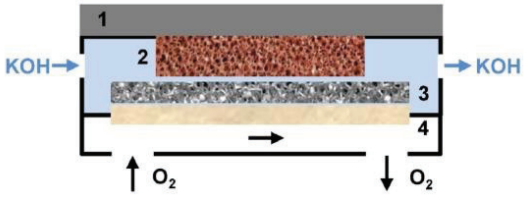

Fig. 1. Schematic illustration of the testing cell: (1) zinc plate, (2) copper foam, (3) nickel foam, (4) oxygen depolarized cathode.

The performance of the cell was characterized at room temperature (RT), unless otherwise stated, using a Basytec CTS battery test system. Voltage–current density (U–i) curves were recorded while increasing the current density by 5 mA cm^{-2} every second. The determination of the battery cycle-life was performed in galvanostatic mode with a current density of 50 mA cm^{-2} related to the geometric surface area of the zinc electrode. According to the given charge efficiency of 90%, which was determined in additional half-cell experiment with the same setup at a current density of 50 mA cm^{-2} and a cut-off potential of zinc vs. RHE of 0.38 V, amounts of transferred electrical charge of 33.5 C during charging and of 30.0 C during discharging were chosen. In order to suppress formation of zinc dendrites or mossy structures during zinc deposition, the charging process was performed at pulsating current (1 s pulse length and 2 s pulse pause) as described by Wang et al. [27].

3. Results and discussion

The voltage–current and power-current characteristics of the zinc-oxygen battery are shown in Fig. 2a. The cell has an open circuit voltage of 1.43 V and still provides a cell voltage of 0.4 V at an extremely high current density of 600 mA cm^{-2}. The peak power density of 270 mW cm^{-2} is reached at a cell voltage of 0.6 V and a current density of 460 mA cm^{-2}. These characteristics are comparable with mechanically rechargeable zinc–air batteries [12,15,28] or hydraulically rechargeable zinc–air fuel cells [14,17–19].

Although nickel is not among the best OER catalysts, the observed overvoltage of the employed nickel foam with high surface area is moderate. Thus a cell voltage of 2.7 V is reached at a charging current density of 600 mA cm^{-2} (Fig. 2b). The corresponding voltage efficiency of the cell as a function of current density is presented in Fig. 2c. While the voltage efficiency remains above 50% for current densities below 100 mA cm^{-2}, it significantly decreases at higher current densities reaching only 23% at 460 mA cm^{-2}, where the peak power density is achieved. The reason for this rapidly decreasing efficiency of the cell is the high overvoltage of both oxygen reactions (Fig. 2d), whereas hardly any overvoltage is observed for the zinc electrode. Surprisingly, the voltage efficiency losses during oxygen reduction at the ODC exceed that of the Ni-foam electrode, which can be possibly attributed to its lower active surface area and long diffusion paths in the pore system [29]. However, the commercial Covestro ODC was originally designed as an electrode for chlor-alkali electrolysis. Therefore better adapted oxygen depolarized cathodes for use in alkaline zinc–air batteries would have positive implications on the cell power.

The influence of operating temperature on the performance of the cell at a current density of 50 mA cm^{-2} is shown in Fig. 2e. After increasing the temperature from RT (22 °C) to 30 °C the voltage efficiency rose slightly by 2%. A further increase of the cell temperature to 40 °C resulted in an initial improvement during the first cycles (Fig. 2e). However, the cyclability of the cell declined dramatically and continuous operation at this temperature was no longer possible. Hydrogen evolution as side reaction, dendrite formation, as well as self-dissolution of deposited zinc could be possible causes for unsatisfactory cycling performance of the cell, which became more pronounced with increasing temperature. These undesired electrode processes could also be the reason for the relatively low charge efficiency of 90%. Therefore, detailed investigation of zinc stability and further improvement of the catalytic activity of oxygen electrodes are required to increase the cell efficiency at lower reaction temperatures.

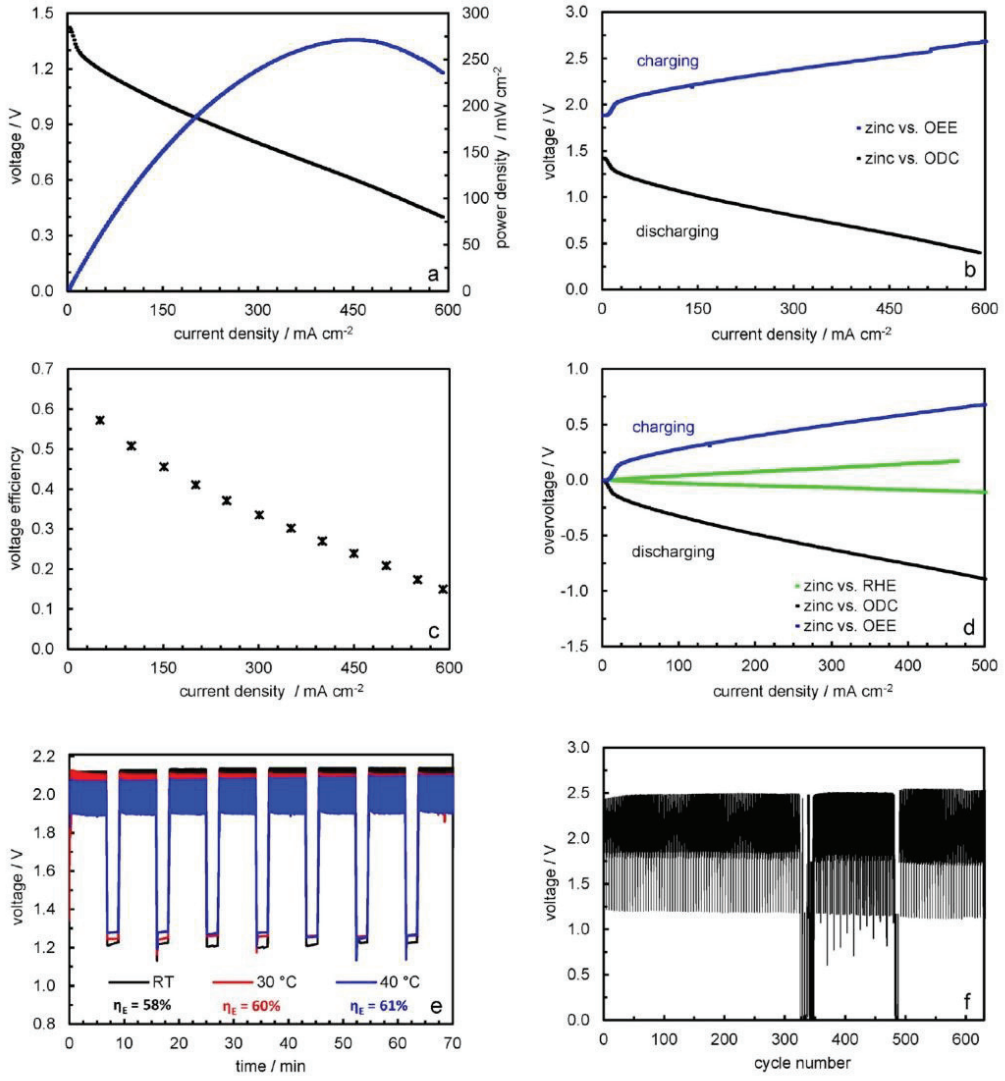

Fig. 2. Characteristics of electrically rechargeable zinc-oxygen cell: (a) voltage–current density and power-current density curves, (b) charge and discharge polarization (U–i) curves, (c) voltage efficiency as a function of current density, (d) overvoltages of the full cell in comparison with overvoltages of a zinc electrode during charge and discharge, (e) influence of operating temperature on cell performance at 50 mA cm^{-2}, (f) cyclic performance of the cell over 600 cycles at RT and 50 mA cm^{-2}.

In Fig. 2f the cycling performance of the cell at RT over 600 cycles is depicted. Initially, stable cyclic behavior was observed for about 250 cycles. Then, inhomogeneous zinc deposition led to repeated short circuits in the cell. A possible reason could be an inhomogeneous electrolyte flow distribution resulting in locally different current densities. However, the cell could be electrochemically reactivated by further oxidation of the electrode. Due to the short circuit between the zinc electrode and the nickel foam, the open circuit voltage for charging mode dropped below the set minimum value (1.8 V, cf. Fig. 2b). Therefore no charging process could proceed and the test system switched automatically back to discharging mode. During this additional oxidation of zinc the dendritic connection between zinc electrode and the OEE could be dissolved. This reactivation of the cell might also have caused an oxidation of the copper foam, which can be recognized by a slightly lower performance of the cell after the second short circuit (Fig. 2f). Coatings of tin, indium or bismuth on the copper foam would prevent it from corrosion and enable a better electrochemical stability of the electrode [30]. Furthermore a modified technical design of the cell e.g. by using a separator between copper and nickel foams or by simplifying the arrangement through use of a bifunctional oxygen electrode [31] and a better flow distribution within it would increase the performance and the lifetime of the battery.

The energy density of the developed zinc-oxygen battery with 2 wt.% ZnO in the electrolyte is still small. Assuming that the total amount of dissolved ZnO from the electrolyte can be deposited as zinc during the charging process, a maximum energy density of 16 Wh kg^{-1} (related to the mass of used electrolyte) would be reached. However, notable improvements of the electrolyte solubility have already been made by other research groups [32–35]. As an example, Briggs et al. [35] showed that during electrochemical dissolution of zinc electrodes in 7 M KOH with

added potassium silicate, a concentration of 2.5 mol L^{-1} (16.6 wt.%) of zincate ions could be reached. With this improved electrolyte capacity, a maximum energy density of 100 Wh kg^{-1} can be achieved, which is already higher than typical values for redox-flow batteries [36,37].

4. Conclusions

In the present contribution we describe an electrochemically rechargeable zinc-oxygen flow cell which is able to operate at very high current densities of up to 600 mA cm^{-2} and delivers a peak power density of 270 mW cm^{-2} with respect to the geometric zinc electrode area. Although short circuits could not be completely prevented, the cell revealed a remarkable cyclability over 600 cycles without the need for exchanging the zinc electrode or the electrolyte. Moreover the presented cell design has further improvement potential, so that even larger-scaled rechargeable flow batteries could be developed on the basis of the demonstrated work.

Acknowledgments

This work was supported by the German Federal Ministry for Economic Affairs and Energy (grant number 03ESP217 E) during the ZnPLUS project. The authors furthermore thank Covestro AG for providing the oxygen depolarized cathodes, Jens-Christian Riede from the Institute of Chemical and Electrochemical Process Engineering, Clausthal University of Technology, and Paul Titscher from the Institute for Particle Technology, TU Braunschweig, for helpful discussions.

References

[1] Y. Li, M. Gong, Y. Liang, J. Feng, J.-E. Kim, H. Wang, G. Hong, B. Zhang, H. Dai, Advanced zinc–air batteries based on high-performance hybrid electrocatalysts, Nat. Commun. 4 (2013) 1–7.
[2] P. Pei, K. Wang, Z. Ma, Technologies for extending zinc–air battery's cyclelife: a review, Appl. Energy 128 (2014) 315–324.
[3] G.X. Zhang, A dual power cell for storing electricity in zinc metal, J. Power Sources 285 (2015) 580–587.
[4] K. Harting, U. Kunz, T. Turek, Zinc–air batteries: prospects and challenges for future improvement, Z. Phys. Chem. 226 (2012) 151.
[5] K.F. Blurton, A.F. Sammells, Metal/air batteries: their status and potential — a review, J. Power Sources 4 (1979) 263–279.
[6] O. Haas, S. Müller, K. Wiesener, Wiederaufladbare Zink/Luftsauerstoff-Batterien, Chem. Ing. Tech. 68 (1996) 524–542.
[7] J.Y. Huot, Chemistry, electrochemisty, and electrochemical applications | zinc, Encyclopedia of Electrochemical Power Sources, Elsevier, Amsterdam 2009, pp. 883–892.
[8] A.R. Mainar, O. Leonet, M. Bengoechea, I. Boyano, I. de Meatza, A. Kvasha, A. Guerfi, J. Alberto Blázquez, Alkaline aqueous electrolytes for secondary zinc–air batteries: an overview, Int. J. Energy Res. (2016).
[9] Y. Li, H. Dai, Recent advances in zinc–air batteries, Chem. Soc. Rev. 43 (2014) 5257–5275.
[10] S. Müller, F. Holzer, O. Haas, Optimized zinc electrode for the rechargeable zinc–air battery, J. Appl. Electrochem. 28 (1998) 895–898.
[11] H. Arai, M. Hayashi, Primary batteries — aqueous systems | zinc–air, Encyclopedia of Electrochemical Power Sources, Elsevier, Amsterdam 2009, pp. 55–61.
[12] P. Pei, Z. Ma, K. Wang, X. Wang, M. Song, H. Xu, High performance zinc air fuel cell stack, J. Power Sources 249 (2014) 13–20.
[13] X.G. Zhang, Secondary batteries — zinc systems | zinc electrodes: overview, Encyclopedia of Electrochemical Power Sources, Elsevier, Amsterdam 2009, pp. 454–468.
[14] S.I. Smedley, X.G. Zhang, A regenerative zinc–air fuel cell, J. Power Sources 165 (2007) 897–904.
[15] G. Savaskan, T. Huh, J.W. Evans, Further studies of a zinc–air cell employing a packed bed anode part I: discharge, J. Appl. Electrochem. 22 (1992) 909–915.
[16] X.-Y. Xie, Z.-F. Ma, X.-X. Ma, Q. Ren, V.M. Schmidt, L. Huang, Preparation and electrochemical characteristics of MnOx–CoTMPP/BP composite catalyst for oxygen reduction reaction in alkaline solution, J. Electrochem. Soc. 154 (2007) B733–B738.
[17] A. Puapattanakul, S. Therdthianwong, A. Therdthianwong, N. Wongyao, Improvement of zinc–air fuel cell performance by gelled KOH, Energy Procedia 34 (2013) 173–180.
[18] C. Jiratchayamaethasakul, N. Srijaroenpramong, T. Bunyangyuen, W. Arpavate, N. Wongyao, A. Therdthianwong, S. Therdthianwong, Effects of anode orientation and flow channel design on performance of refuelable zinc–air fuel cells, J. Appl. Electrochem. 44 (2014) 1205–1218.
[19] S. Smedley, X.G. Zhang, Secondary batteries — metal-air systems | zinc–air: hydraulic recharge, Encyclopedia of Electrochemical Power Sources, Elsevier, Amsterdam 2009, pp. 393–403.
[20] H. Ma, B. Wang, Y. Fan, W. Hong, Development and characterization of an electrically rechargeable zinc–air battery stack, Energies 7 (2014) 6549.
[21] I. Moussallem, J. Jörissen, U. Kunz, S. Pinnow, T. Turek, Chlor-alkali electrolysis with oxygen depolarized cathodes: history, present status and future prospects, J. Appl. Electrochem. 38 (2008) 1177–1194.
[22] I. Moussallem, S. Pinnow, N. Wagner, T. Turek, Development of high-performance silver-based gas-diffusion electrodes for chlor-alkali electrolysis with oxygen depolarized cathodes, Chem. Eng. Process. 52 (2012) 125–131.
[23] P.N. Ross, A novel zinc–air battery for electric vehicles, Battery Conference on Applications and Advances, IEEE, Long Beach 1995, pp. 131–133.
[24] P.N.J. Ross, Feasibility study of a new zinc–air battery concept using flowing alkaline electrolyte, 21st Intersociety Energy Conversion Engineering Conference, San Diego 1986, pp. 1–28.
[25] P.N. Ross, A new concept in an electrically rechargeable zinc–air alkaline battery, Battery and Electrochemical Contractors' Meeting, Tysons Corner 1987, pp. 1–8.
[26] A.G. Briggs, N.A. Hampson, A. Marshall, Concentrated potassium zincate solutions studied using laser Raman spectroscopy and potentiometry, J. Chem. Soc. Faraday Trans. 2 Mol. Chem. Phys. 70 (1974) 1978–1990.
[27] K. Wang, P. Pei, Z. Ma, H. Chen, H. Xu, D. Chen, X. Wang, Dendrite growth in the recharging process of zinc–air batteries, J. Mater. Chem. 3 (2015) 22648–22655.
[28] T. Huh, G. Savaskan, J.W. Evans, Further studies of a zinc–air cell employing a packed bed anode part II: regeneration of zinc particles and electrolyte by fluidized bed electrodeposition, J. Appl. Electrochem. 22 (1992) 916–921.
[29] S. Pinnow, N. Chavan, T. Turek, Thin-film flooded agglomerate model for silver-based oxygen depolarized cathodes, J. Appl. Electrochem. 41 (2011) 1053–1064.
[30] R.F. Ngamga, Electrochemical Reaction of the Zn/Zincate/ZnO System, Institute of Inorganic Chemistry, Graz University of Technology, 2011.
[31] D. Wittmaier, N. Wagner, K.A. Friedrich, H.M.A. Amin, H. Baltruschat, Modified carbon-free silver electrodes for the use as cathodes in lithium–air batteries with an aqueous alkaline electrolyte, J. Power Sources 265 (2014) 299–308.
[32] A.L. Zhu, D. Duch, G.A. Roberts, S.X.X. Li, H. Wang, K. Duch, E. Bae, K.S. Jung, D. Wilkinson, S.A. Kulinich, Increasing the electrolyte capacity of alkaline Zn–air fuel cells by scavenging zincate with $Ca(OH)_2$, ChemElectroChem 2 (2015) 134–142.
[33] E. Frackowiak, K. Jurewicz, Improvement of secondary zinc electrodes, in: F. Lapicque, A. Storck, A.A. Wragg (Eds.), Electrochemical Engineering and Energy, Springer US, Boston, MA 1994, pp. 41–46.
[34] C. Debiemme-Chouvy, J. Vedel, Supersaturated zincate solutions: a study of the decomposition kinetics, J. Electrochem. Soc. 138 (1991) 2538–2542.
[35] A.G. Briggs, N.A. Hampson, A. Marshall, Concentrated potassium zincate solutions studied using laser Raman spectroscopy and potentiometry, J. Chem. Soc. Faraday Trans. 70 (1974) 1978–1990.
[36] G. Kear, A.A. Shah, F.C. Walsh, Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects, Int. J. Energy Res. 36 (2012) 1105–1120.
[37] L. Li, S. Kim, W. Wang, M. Vijayakumar, Z. Nie, B. Chen, J. Zhang, G. Xia, J. Hu, G. Graff, J. Liu, Z. Yang, A stable vanadium redox-flow battery with high energy density for large-scale energy storage, Adv. Energy Mater. 1 (2011) 394–400.